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EMF MEASUREMENTS IN RIMMING STEEL MELTS

Formation of the skin layer free from blowholes

Solidified steel melts of effervescing nature are characterized by an ingot structure which shows a sound skin layer and, adjacent to it, an outer wreath of blowholes. Further inside, the ingot reveales in general an inner wreath of blowholes, which is clearly shown up against the outer one, as well as non-uniform shrinkage cavities in the upper third portion. However, on further consideration, the solid skin layer turns out a disturbed solidification structure: microcavities are constituting blowhole traces which finally issue in the slightly upward sloping macrochannels of the outer wreath of blowholes (1). The thickness of the skin layer and its inclusion content are determining the surface quality of the finish-rolled product. Consequently, the knowledge of those factors influencing the early stage of the carbon/oxygen ebullition reaction is of special importance technically.

First, it must be stated that the formation of blowhole channels begins at a moment when the gas bubbles growing at the interface of solid/liquid are trapped and outrun by the progressive solid phase prior to breaking away and rising out of the liquid steel. It may be estimated from solidification laws and usually found skin thicknesses of about 10 mm that this transitional stage is reached already with filling up the mould. This is in line with the observation that the thickness of the layer is constant and not depending upon the ingot height. So, the skin layer free from blowholes is formed with first boiling whilst subsequent boiling out remains without any influence on the skin structure.

The solubility of CO in crystallized iron is practically nil (2). It, therefore, was assumed for a long time that the intensity of the carbon/oxygen reaction during solidification could not fail to involve the formation of a rim free from blowholes. As against that it is known from steel making practice that, with excessively deoxidized steel before casting, ingots are produced of which the outer wreath of blowholes is set free in the soaking pit by scaling. Melts of this kind tend to climb. On casting semi-killed qualities, blowholes are found in the ingot surface if the melt contains excessive amounts of oxygen due to insufficient deoxidation.

A closer investigation into the factors influencing the beginning ebullition process of unkilled steels originates from Stein, Kootz and Wick who discovered in 1966 that the thickness of the skin layer increases with progressive oxygen oversaturation of the ladle melt (3). Based on similar considerations, Selivanov and Korotkikh developed in 1973 a casting diagram for unkilled steels (4) which is shown in figure 1. This diagram states the expected thickness of the skin layer free from blowholes in dependence upon the carbon and oxygen contents of the ladle melt as well as the casting temperature and the rising rate. It appears that small variations of the oxygen content in the melt have a great influence on the thickness of the skin layer.

The quantitative conclusions of both mentioned studies are questionable in that the oxygen content of the melt was analyzed chemically as the total oxygen content of killed samples post mortem. Furthermore, it should be taken into consideration that the casting diagramm of Selivanov and Korotkikh can only be used in the metallurgical practice if the dissolved oxygen content of the melt is directly accessible. It, therefore, seemed useful to insure and extend the range of knowledge by electrochemical oxygen measurements in unkilled steel melts. It should be noted here that the results available hitherto are still incomplete.

The EMF measurements were carried out on industrial 185 tons melts in the casting ladle after tapping, simultaneously, one sample was taken every time. The melts were top-poured into 11 tons moulds at a rising rate of 1 m min^{-1}. About 1 minute after filling EMF measurements were performed also in the moulds. The immersion depth of the cell into the molten metal was of 0.25 m. No further samples were taken from the mould.

Figure 2 shows the results of the electro-chemical oxygen measurements. The unkilled steel melts showed a uniform basic composition of 0.30 to 0.40 % Mn, about 0.010 % P and 0.030 % S; the liquidus temperature was rated at 1520 ^{o}C and the casting temperature at 1565 ^{o}C. The carbon/oxygen equilibrium was calculated according to the approach of Nilles (5) for the limiting conditions $(p_{CO} + p_{CO_2}) = 1$ atm. It should still be added that oxygen is blown upon the pouring stream by means of an annular nozzle if the carbon content of the melt exceeds the limit of 0.12 %.

In accordance with the refining behaviour of steel baths, the electro-chemical measurements of the oxygen in casting ladles show decreasing oxygen activities with increasing carbon contents. However, a relatively large variation width of the oxygen activity in the ladle melt applies to a specified carbon content. This result is to be expected since the previous deoxidation of the melt with tapping generally is undertaken without knowing its oxygen content. Thereby, the previous deoxidation needs to be graded in such manner that a good distance to the equilibrium at 1 atm total pressure is maintained and, consequently, the ladle melt is oversaturated with CO. In order to adhere to these limiting conditions, melts with elevated carbon content must be blown with oxygen during casting as already was mentioned.

In figure 2 , related ladle and mould measurements were joined with a line; thereby, the oxygen activity measured in the mould was correlated to a carbon content in compliance with the stoichiometric conversion into CO. It becomes evident that the oxygen activity in the mould closely approaches the state of equilibrium at p = 1 atm shortly after filling up. This finding signifies that the CO oversaturation is already reduced to a great extent within the first boiling period.

In order to verify this relationsship, three small melts of 1.5 tons in weight were molten in the induction furnace and subsequently bottom cast. Due to the moderate weight of the melts, elevated casting temperatures had to be chosen. In the main, these three melts differed by the adjusted oxygen contents and the rising rate. After solidification, the ingots were cut open to measure the thickness as well as the inclusion content of the blowhole-free rim. Table 1 groups the test data.

It is apparent from the test data that the thickness of the skin layer free from blowholes increases with increasing CO oversaturation of the ladle melt and decreasing rising rate. In the absence of CO oversaturation subcutaneous blowholes are formed. These results are qualitatively in line with the casting diagram of Selivanov and Korotkikh in figure 1. The measuring of the inclusion content of the skin layer did not result in a homogeneous picture. According to Täffner and Trömel, "normal" boiling should lead to low inclusion values (6). The elucidation of this question requires further systematical examinations. Moreover, it is not sufficiently known how the different sulphur contents and carbon/manganese ratios are affecting the first boiling stage of the melt.

In the early boiling stage, two streams of material are contributing to the growth of the gas bubbles at the solid/liquid interface: the gas bubbles take up CO at their basis from the concentration boundary layer; the circulating and oversaturated melt furnishes CO through the front of the bubbles. Now, it is assumed that the solidification front outruns the gas bubbles with forming the outer wreath of blowholes when the CO pumping flux of the remaining liquid steel breaks down with the progressive reduction of the CO oversaturation. This condition is reached at a melt depth "h" when the pressure in the macroscopic bubble is equal to the sum of atmospheric and ferrostatic pressure:

$$(a_C \cdot a_O)_{eq} = K \cdot p_{CO} = K\,(p_o + \varrho\, g\, h_{eq}) \qquad (1)$$

An analogous equation to relation (1) is applicable for the considerably higher $(a_C \cdot a_O)$ product adjusted in the ladle melt whereby the height "h" represents a virtual factor. By substraction, it follows

$$(a_C \cdot a_O)_{ladle} - (a_C \cdot a_O)_{eq} = K \cdot \varrho \cdot g \cdot \Delta h \qquad (2)$$

With uniform rising rate in the mould, the further result is

$$(a_C \cdot a_O)_{ladle} - (a_C \cdot a_O)_{eq} = K \cdot \varrho \cdot g \cdot v_{St} \cdot \Delta t \qquad (3)$$

Within the period Δt, the skin layer free from blowholes of the thickness ξ is formed in dependence upon the melt overheating ΔT so that

$$(a_C \cdot a_O)_{ladle} - (a_C \cdot a_O)_{eq} = K\,\varrho\, g\, v_{St} \cdot \varphi(\xi, \Delta T) \qquad (4)$$

As the carbon content of the ladle melt is almost corresponding to the carbon content of the mould melt, it follows lastly

$$a_{O,\mathrm{ladle}} - a_{O,\mathrm{eq}} = \Delta a_O = \frac{K \varrho g v_{St}}{a_C} \cdot \varphi(\xi, \Delta T) \qquad (5)$$

Thus, these plausibility considerations result in a final equation which covers all influencing factors on the thickness of the skin layer on which is based the casting diagram of Selivanov and Korotkikh: carbon content and oxygen content, rising rate and melt overheating.

There is a suggestion to derive, according to equation (5), the rule for the steelmaking practice that the oxygen content should be chosen as high as possible in order to obtain a skin layer as thick as possible. Here is a limit to this measure with carbon contents below 0.12 %: wild boiling and ebullition under boot-leg formation occur with excessive oxygen values. Consequently, an optimum ladle oxygen content should apply to steel melts of effervescing nature which ought to be according to the measurements available with reference to the equilibrium in the mould at $(a_C \cdot a_O)_K$ = 0.0018 approximately

$$a_{O,\mathrm{ld},\mathrm{Opt.}} = \frac{0.0018}{\% \, C_{\mathrm{ld}} - \frac{12}{16} \cdot 0.014} + 0.014 \qquad (6)$$

This equation is based on the assumption that an optimum result requires the reduction of about 0.014 % of oxygen with forming CO in the early boiling stage independently of the carbon content.

The optimum ladle oxygen contents according to equation (6) are recorded in figure 3. From measurements by Halberg (7) , the following applies to LD steel melts

$$(\% \, C \, . \, a_O)_{LD} \cong (35 \pm 6) \, . \, 10^{-4} \qquad (7)$$

This relation also is included in figure 3. The two curves intersect at 0.11 % of carbon. With lower carbon contents, the converter melt must be deoxidized before casting; higher carbon contents require oxygen blowing upon the pouring stream between the ladle and the mould. The aluminum amount in grams per ton of steel to be used for the previous deoxidation will be at the best

$$m_{Al} = \frac{54}{48} \, (a_{O,LD} - a_{O,ld,Opt.}) \, . \, 10^4 \qquad (8\ a)$$

or after substitution of the equations (6) and (7)

$$m_{Al} = \frac{54}{48} \left(\frac{35}{[\%C]} - \frac{18}{[\%C] - \frac{12}{16} \, . \, 0.014} - 140 \right) \qquad (8\ b)$$

The equation (8) is applicable for carbon contents from about 0.035 to 0.10 %.

In steelmaking plants, the aluminum amounts usually added are somewhat higher than those calculated from equation (8 b). The reason is that the free pouring stream absorbes oxygen from the ambient atmosphere. This effect was neglected with the above considerations as precise measurements are not available hithero.

On the described limiting conditions, the reliable adjustment of the undoubtly existing optimum oxygen content logically calls for the introduction of the electro-chemical oxygen measuring method in steelmaking practice. Thereby, several process technological solutions are possible:

1. The deoxidation of the melt before tapping ~~casting~~ is effected in accordance with its oxygen content determined by electrochemical measuring in the furnace.

2. According to the result of the electro-chemical determination of the oxygen in the ladle, trimming additions in the form of boiling energizers or in the form of aluminum are introduced into the mould.

3. The rising rate is fixed in compliance with the oxygen content of the ladle melt; by way of example, this method is applicable for ladles with slide gate by selecting the change conus accordingly.

4. The optimum oxygen content and the desired casting temperature are adjusted by means of a ladle metallurgical process.

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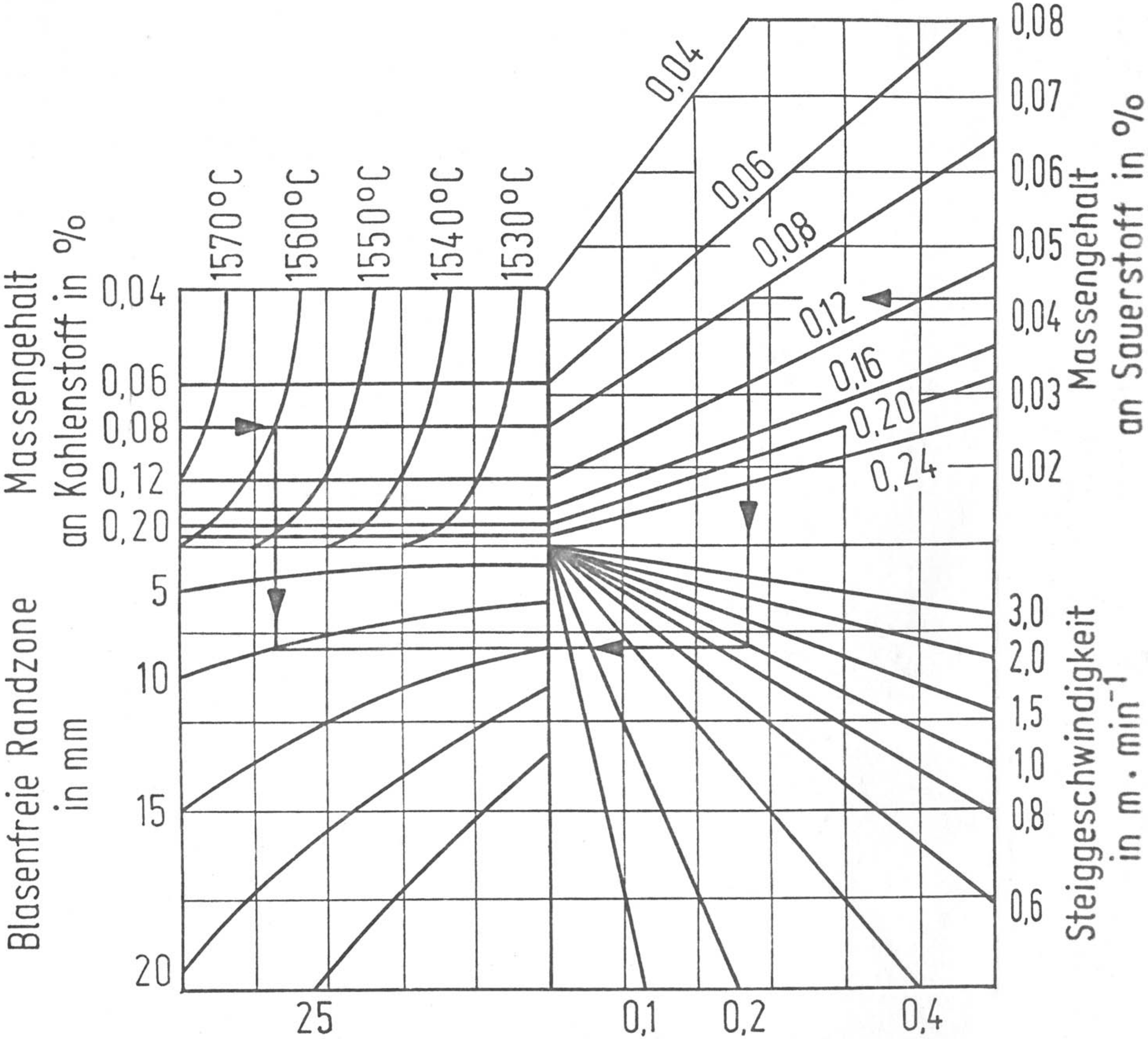
Vergießen unberuhigter Schmelzen

(1,5 t Versuchsschmelzen)

Schmelze / Block		1	2	3
Gießpfanne	Kohlenstoff	0,10 %	0,08 %	0,07 %
	Mangan	0,41 %	0,34 %	0,43 %
	Phosphor	n. b.	0,020 %	0,025 %
	Schwefel	n. b.	0,022 %	0,027 %
	Sauerstoffaktivität	0,030	0,023	0,044
Gießdaten	Gießtemperatur	1604 °C	1608 °C	1629 °C
	Steiggeschwindigkeit	0,70 m min^{-1}	0,70 m min^{-1}	0,17 m min^{-1}
Kokille	Sauerstoffaktivität	0,022	0,022	0,037
Auswertung	Sauerstoffabbau Δa_0	− 0,008	− 0,001	− 0,007
	Blasenfreie Randschicht	14 mm	4 mm	36 mm
	Flächenbezogener Einschlußgehalt	0,21 %	0,20 %	0,17 %



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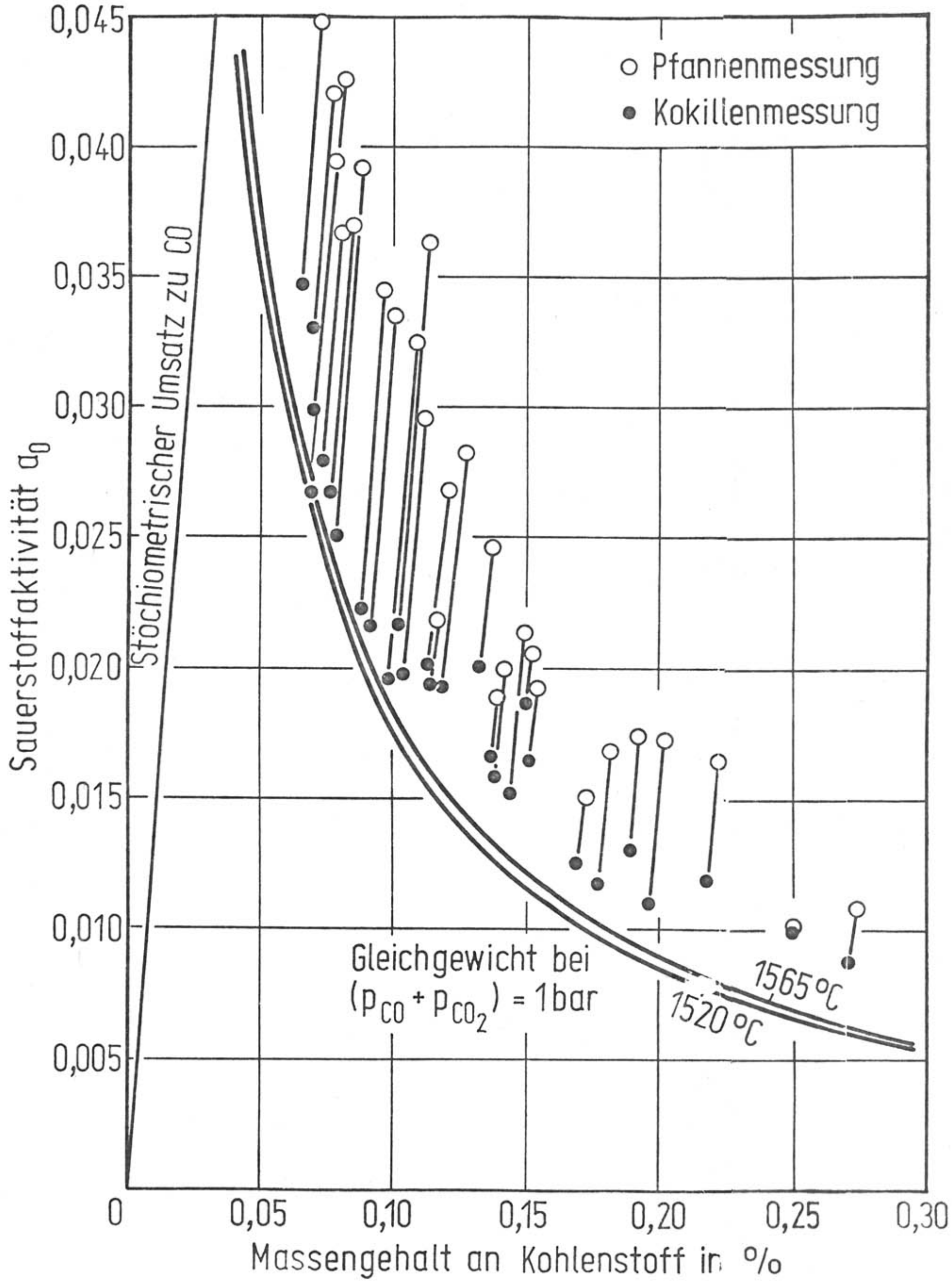
Gießdiagramm
für unberuhigte
Stahlschmelzen
(nach Selivanov und
Korotkikh)

Stahleisen
Met. A.



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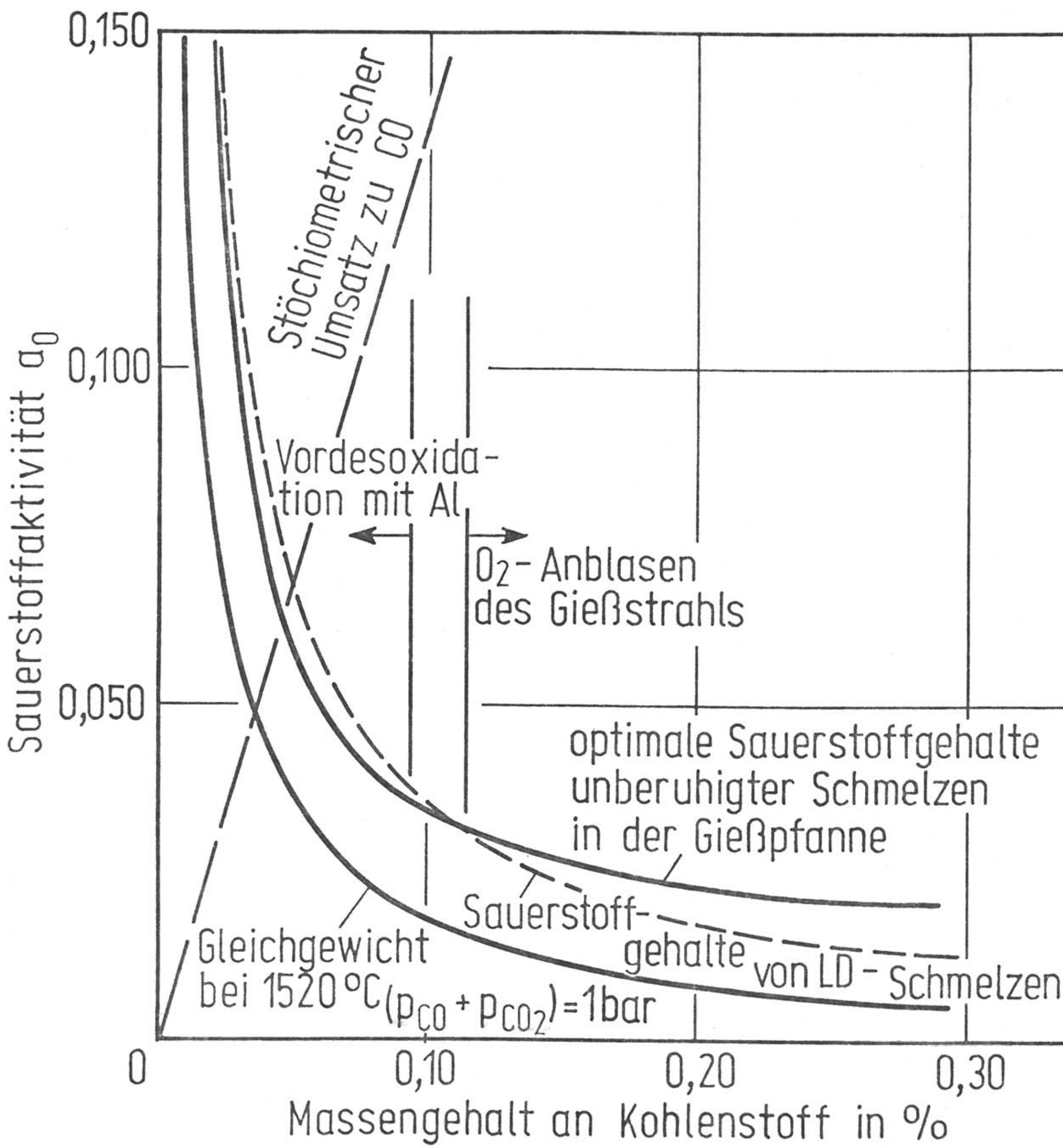
Abbau der Sauerstoffübersättigung in unberuhigten Schmelzen beim Loskochen in der Kokille

Stahleisen
Met. A.



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Vordesoxidation und Nachoxidation unberuhigter Stahlschmelzen

Stahleisen
Met. A.